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FUEL

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This invention relates generally to fuels for high-compression, spark-ignition engines and more particularly to fuels in which there is less tendency to cause autoignition when high compression internal combustion engines are operated thereon than is the case when present well-known fuels are used under similar operating conditions.

It has long been recognized that there are two distinguishable but related combustion phenomena that act as barriers to the utilization of higher compression ratios in internal combustion spark-ignition engines. By preventing the use of higher compression ratios or higher pressures attained by other means, these two barriers prevent the attainment of fuel economy and efficiency that would otherwise be possible.

These two barriers are: first, knock, and second, autoignition. Substantial progress has been made in the control of knock through the discovery of the antiknock effect of lead alkyls such as tetraethyl lead and through progress in the manufacture of hydrocarbon fuels having high antiknock value. This invention has as its principal object the reduction or suppression of autoignition.

In order to make clear the object of this invention it is desirable to distinguish between the phenomena of autoignition, preignition and knock. Autoignition as the name implies, is an ignition of the mixture by some means other than the normal ignition spark. It may occur in advance of the normal flame front after the charge has been ignited by the normal spark or it may occur before the time of normal ignition. In the latter case autoignition and preignition are the same phenomenon.

When autoignition is occurring in an engine, the observer will often find that the electric-spark ignition switch can be shut off and the engine operation will continue unaffected. This is frequently caused by incandescent particles of the combustion chamber deposits which are undergoing vigorous oxidation either on the combustion chamber walls or in the gaseous phase and which ignite the fresh fuel-air mixture during the compression event either after, or in advance of the electric spark at the spark plug. When autoignition occurs in its most objectionable form, namely, prior to ignition, the observer hears a sharp, high-pitched sound—"knock"—similar to that which might be expected if the spark were advanced far beyond the normal setting.

Autoignition and normal ignition differ from the phenomenon of knock in that these phenomena relate to the simultaneous inflammation of relatively small portions of the entire charge and in that they do not develop local pressures of appreciable magnitudes. The phenomenon of knock, on the other hand, is associated with the development of comparatively high local pressures resulting from the rapid combustion of comparatively large percentages of the charge in the engine. This combustion results from a compression-ignition process occurring in the unburned fuel-air mixture ahead of the normal flame front, and differs from autoignition in that ignition takes place simultaneously in a relatively large part of the charge eliminating the progressive type of burning process which characterizes normal combustion. In fact, the ignition of the portion of the charge which knocks is so sudden that local pressures develop in this part of the charge and the equalizing of these pressures throughout the combustion space sets up sound waves in the burned charge that are responsible for the sound of knock.

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Knock does not occur in all explosions because of the so-called ignition lag which is characteristic of all fuel-air mixtures. By the term "ignition lag" is meant the time interval during which a given fuel-air mixture can exist at a given temperature and pressure without undergoing ignition. Obviously then, knock may be reduced in intensity or even eliminated entirely by increasing sufficiently the rate of inflammation of the charge. But, when this is done, the engine emits disagreeable noises and is said to be rough, that is, unless it is especially designed to take extremely heavy loads. In other words, the high pressures which develop in extremely short times shock the mechanical system.

One method of decreasing the time interval during which the fuel-air mixture is subjected to high pressures and temperatures is to ignite the charge at several points simultaneously. When engine deposits produce the multiple ignition, the number of ignition points vary considerably from one explosion to the other and the rough operation is extremely objectionable. This is because the engine is suffering from a shock type of excitation that varies erratically in its severity and it is on this account that autoignition is to be avoided even though it occurs after the normal ignition spark.

The present invention has as its principal object the reduction or suppression of autoignition in spark-ignition engines. In accordance with the invention, this object is accomplished by the use of fuels or gasolines containing addition agents which affect the chemical composition and

oxidation characteristics and to some extent the weight and other mechanical characteristics of the combustion chamber deposits.

Acting upon the aforesaid concept of the causes of autoignition, an investigation has been made of the oxidation characteristics of various combustion chamber deposits and of various mixtures of inorganic compounds with carbon. Of particular significance, it has been found that certain compounds of lead commonly found in combustion chamber deposits have an unusual and unexpected effect upon the ignition and burning characteristics of carbon.

Gasolines used today in automobile engines commonly contain a small amount of a lead alkyl antiknock compound, tetraethyl lead being employed commercially. Common automotive fuels may contain up to about 3 cc. of tetraethyl lead per gallon of gasoline. Aviation gasolines commonly contain substantially higher concentrations of tetraethyl lead. Along with the tetraethyl lead small amounts of various volatile alkyl halides are commonly employed, for example, bromides and chlorides such as ethylene dibromide and ethylene dichloride. When a gasoline containing lead tetraethyl, and the bromide and/or chloride compounds is used as a fuel in internal combustion engines it is found that the deposits on the walls of the combustion chamber contain carbon and various lead compounds such as lead bromide, basic lead bromide, lead chloride, basic lead chloride, lead sulfate and basic lead sulfate. Lead compounds such as these and also engine deposits from leaded-gasolines exert a catalytic effect and not only lower the ignition temperature of carbon, but they impart to the mixture an ability to continue to burn after the primary source of heat is removed that is not had by carbon alone.

The effect of several lead compounds on ignition temperature is given in table below in which the ignition temperatures of mixtures containing 10 per cent of various substances and 90 per cent of carbon, in the form of carbon black, were determined under certain controlled conditions:

Table

Material Tested	Chemical Formula	Ignition Temperature, ° F.
Pure Carbon	C	Over 1200
Combustion chamber deposit from engine operated on gasoline containing Ethyl fluid.		680–750
Individual lead compounds known to exist in combustion chamber deposits:		
Lead bromide	$PbBr_2$	[1] 720
Basic lead bromide	$PbO.PbBr_2$	[1] 727
Lead chloride	$PbCl_2$	[1] 727
Basic lead chloride	$PbO.PbCl_2$	[1] 727
Lead sulphate	$PbSO_4$	[1] 939
Basic lead sulphate	$PbO.PbSO_4$	[1] 950

[1] Results obtained by averaging results of four separate determinations.

As indicated in this table, the halogen compounds of lead are extremely active in promoting the oxidation of carbon. Accordingly, the presence of these compounds in combustion chamber deposits will tend to produce autoignition when other conditions are favorable.

The Campbell application, Serial No. 475,003, filed February 6, 1943, discloses and claims use of small amounts of volatile liquid phosphorus compounds in leaded-gasolines for use in internal combustion spark-ignition engines in order to inhibit or prevent the activating effect of lead on ignition of carbon. In this way autoignition is inhibited or prevented.

I have found that phosphorus compounds differ greatly in their effect on the antiknock activity of the tetraethyl lead or other lead alkyl and that most of them tend to depreciate the antiknock activity of tetraethyl lead or other lead alkyl. I have also discovered that trimethyl phosphate and trimethyl phosphite are particularly advantageous in that they have relatively little effect in depreciating the antiknock value of tetraethyl lead (or other lead alkyl) and at the same time have a powerful effect in preventing autoignition. I have also discovered that the halide compound and/or compounds normally employed in leaded-gasolines may be replaced by the phosphorus-compound or compounds with beneficial effect.

Relatively small amounts of the compounds of phosphorus are all that are required in leaded-gasolines in order to correct the tendency toward autoignition. In many instances from 1 to 3 cc. of the phosphorus compound per gallon of gasoline have been used with satisfactory results. In general amounts less than about .3% by volume are employed. The larger amounts tend to cause an excess deposit on the engine valves and this is undesirable.

It appears as a result of my investigations that trimethyl phosphate is the better additive for gasolines containing 2 cc. or more of tetramethyl lead per gallon and that trimethyl phosphite is preferable with lower concentrations of lead.

Ordinary leaded-gasolines contain halides such as ethylene dibromide and/or ethylene dichloride in small amounts on the order of one or two cubic centimeters per gallon of gasoline. I have found that the halide may be eliminated in whole or in part and replaced with the phosphorus compounds with beneficial effect as regards the antiknock activity of the tetraethyl lead.

I claim:

1. A leaded-gasoline containing a small amount of at least one of the group consisting of trimethyl phosphate and trimethyl phosphite.

2. A leaded-gasoline containing a small amount of trimethyl phosphate.

3. A leaded-gasoline containing a small amount of trimethyl phosphite.

4. A leaded-gasoline containing 1 to 3 cc. per gallon of at least one of the group consisting of trimethyl phosphate and trimethyl phosphite.

5. A liquid fuel for spark-ignition internal combustion engines, consisting of hydrocarbons of the gasoline boiling range, a small amount of a volatile lead alkyl compound, and at least one of the group consisting of trimethyl phosphate and trimethyl phosphite in amount less than .3% of the fuel by volume.

6. A leaded-gasoline containing 1 to 3 cc. per gallon of trimethyl phosphate.

7. A leaded-gasoline containing 1 to 3 cc. per gallon of trimethyl phosphite.

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